Recent advances in the application of biochar for wastewater treatment: A review (#42777)

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- Methods described with sufficient detail & information to replicate.
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Recent advances in the application of biochar for wastewater treatment: A review

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In the past decade, researchers have carried out a massive amount of research on the application of biochar for removing pollutants in aqueous solution. As an emerging adsorbent with potential efficacy, biochar has shown excellent advantages of broad sources of feedstocks, easy preparation, low-cost, and favorable surface properties. This review provides an overview of recent advances in biochar application and modification technologies, including a brief discussion on adsorption mechanisms involved in different pollutants removal. Furthermore, environmental concerns of biochar that need to be paid attention to and future research directions are put forward, to promote its practical application in wastewater treatment.

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Abstract

In the past decade, researchers have carried out a massive amount of research on the application of biochar for removing pollutants in aqueous solution. As an emerging adsorbent with potential efficacy, biochar has shown excellent advantages of broad sources of feedstocks, easy preparation, low-cost, and favorable surface properties. This review provides an overview of recent advances in biochar application and modification technologies, including a brief discussion on adsorption mechanisms involved in different pollutants removal. Furthermore, environmental concerns of biochar that need to be paid attention to and future research directions are put forward, to promote its practical application in wastewater treatment.

Introduction

Biochar, with rich carbon content, is a thermal decomposition product derived from biomass under a condition that lacks oxygen (Sohi, 2012). These innovations about converting organic matters into valuable materials such as biochar and practical applications have drawn the attention of the relevant fields. Initial studies focused on the ability of different biochars to absorb inorganic nutrients as soil amendments to improve soil quality or promote other environmental services (Sanroman et al., 2017). Numerous researches have shown the interests of biochar in improving soil properties and increasing crop yield (Awad et al., 2017), which ultimately contributes to soil carbon sequestration (Windeatt et al., 2014) and the reduction of greenhouse gases. In recent years, progresses in the production of various biochars have improved their performance and expanded their application in multidisciplinary fields. Biochar research is being carried out in increasing countries, with the specific use varying widely, depending on the feedstock, production techniques, the purpose of use, and the local economy and environment (Tan et al., 2015).

Wastewater treatment is one of the emerging subsets of biochar applications. Due to its properties of large pore volume and specific surface area, rich organic carbon content and mineral components, abundant and diverse functional groups, biochar displays prominent adsorption ability for both inorganic and organic contaminants in aqueous solution (Ahmad et al., 2014). Ion exchange, membrane separation, chemical precipitation, adsorption using activated carbon, etc. are traditional techniques to remediate persistent contaminants from the aqueous phase. These old methods have disadvantages such as high-cost and inevitable generation of a large number of chemical residues with no economic value (Oliveira et al., 2017). In contrast, biochar can be produced from a vast variety of feedstocks, mainly agricultural biomass and solid waste, such as wood, leaves, rice husks and straw, bagasse, manure, and many others (Ahmad et al., 2014; Nanda et al., 2016; Thornley et al., 2009). The resources of feedstocks are among the wealthiest renewable resources in the ecosystem (Yao et al., 2012; Shen et al., 2012; Xu et al., 2013), making biochar an easy-to-get and renewable adsorbent and appropriate for low-income communities.

In an extended period, the wastewater treatment and water purification field have used activated carbon to remove water pollutants. However, activated carbon has its practical limits, such as lower yield and higher energy consumption, making it as much as 20 times more costly than biochar (Thompson et al., 2016). In many cases, biochar shows favorable pollutants removal efficiency as activated carbon has, or even indicates higher removal quantity than activated carbon, owing to the smaller size of biochar particles which could adsorb more trace organic pollutants in contrast to the granular activated carbon (Ulrich et al., 2017). In wastewater, biochar has twice the removal ability of total chemical oxygen demand (COD) as much as activated carbon, since macropores in biochar are not so easy to be clogged and could capture more particulate matter (Huggins et al., 2016). Anyhow, biochar displays more environmental profits in aspects of energy demand for production and greenhouse gases emission. Biochar can be used as a substitute for activated carbon to meet the increasingly stringent ecological requirement. Moreira et al. (Moreira et al., 2017) also proved this by reviewing a comparison of the global environmental impacts in four categories between different biochar systems derived from several feedstocks and the production process of activated carbon. Positive values imply damaging burdens, and negative ones indicate environmental credits, which partly counteract the environmental impacts. Although higher energy requirements in the pyrolysis process of biochar lead to unfavorable results compared with activated carbon production, these impacts could be offset by higher environmental credits from other aspects (climate change, terrestrial acidification, fossil depletion). As a whole, biochar exhibits lower effects in its production and application than activated carbon. Biochar can be an alternative adsorption material that is more sustainable for today’s environmental purposes.

Biochar is a by-product of thermochemical transformation such as pyrolysis, hydrothermal carbonization, gasification, torrefaction, etc. (Meyer et al., 2011). Reports have shown that the physicochemical properties such as pore size, specific surface area, element composition depend on pyrolysis conditions and feedstock types (Ahmad et al., 2014; Uchimiya et al., 2013; Nachenius et al., 2013), making vital implications on its efficiency and suitability in removal of targeted contaminants (Oliveira et al., 2017), including various organics (e.g., dyes, phenols, polycyclic aromatic hydrocarbons (PAHs), agrochemicals, antibiotics), and a series of inorganics (e.g., heavy metals, phosphate, nitrate, ammonia, fluoride) from wastewater (detailed discussion is given in the section "Application of biochar in wastewater treatment").

At present, biochar is having more applications in wastewater treatment because of its distinctive properties and economic and environmental benefits. This paper reviews the recent advances on wide biochar applications in wastewater treatment, containing a brief discussion on the mechanisms as the adsorption happens in the removal of certain inorganic and organic pollutants. Moreover, this review covers briefly the various modification approaches of biochar based on different goals and explains how the modification alters the structure and surface properties, as well as how much the treatment enhances the removal efficiency. Furthermore, this review also highlights the remained environmental concerns and future research directions of biochar, with possible solutions put forward.

Survey methodology

The literature reviewed in this paper was obtained on databases of ScienceDirect, Web of Science and the Chinese journal databases CNKI. The keywords used to search for literature on the databases are as follows: biochar, feedstock, cellulose, lignin, pyrolysis or carbonization associated with the raw materials and methods for biochar production; industrial, agricultural, pharmaceutical, heavy metals, dyes, pesticides, antibiotics, polycyclic aromatic hydrocarbons (PAHs) or trace pollutants reflecting the application of biochar; precipitation, complexation, electrostatic effect, hydrophobicity or chemical bonds referred to mechanisms involved in the adsorption process; porosity, specific surface area, functional groups, magnetization or biochar-based composites related to modification techniques of biochar. Besides, literature research was specially conducted within the papers on the "Special Issue on Biochar: Production, Characterization and Applications - Beyond Soil Applications" published on "Bioresource Technology".

Adsorption mechanisms

The adsorptive ability of biochar for removing a broad series of heavy metals and organic contaminants has been well documented. Yet, there is a lack of studies on corresponding adsorption mechanisms for target contaminants. It is needed to determine the fundamental mechanisms during the adsorption to evaluate the removal efficacy and achieve the biochar field application. Adsorption of different pollutants is dominated by different mechanisms, which are strictly related to the properties of both pollutants and biochar, mainly their surface properties. Here, the dominant mechanisms involved in contaminant removal are illustrated in Figure 1.

Heavy metals

In the environment, heavy metals are ubiquitous (Järup & Åkesson, 2009). They can accumulate in organisms, causing potentially damaging effects to the ecosystem and human health. Anthropogenic activities such as smelting, mining, and electronic manufacturing emission increase the concentration of heavy metals in aqueous solution (Li et al., 2017).

Biochar adsorption has been suggested in heavy metals removal from contaminated water. Primary mechanisms of heavy metals adsorption vary depending on their valence states under different solution pH conditions (Li et al., 2017). On the basis of literature, four mechanisms dominating heavy metals adsorption from water by biochar are proposed as follows (Qian et al., 2015; Tan et al., 2015; Li et al., 2017): (i) electrostatic attraction between heavy metals and biochar surface; (ii) Ion exchange between alkaline metals or protons on biochar surface and the heavy metals; (iii) complexation with π electron-rich domain or surface functional groups; and (iv) coprecipitation to form insoluble compounds. Here, specific adsorption examples are used to explain each mechanism.

The solution pH could strongly influence the surface charge of biochar. pH_{PZC} is the solution pH at which the biochar surface net charge is zero. Biochar is positively charged at solution pH < pH_{PZC} and binds metal anions such as $HAsO_4^{2-}$ and $HCrO_4^-$. On the contrary, biochar is negatively charged at solution pH > pH_{PZC} and binds metal cations such as Hg^{2+}, Pb^{2+}, and Cd^{2+} (Li et al., 2017). These processes are the electrostatic attraction — for instance, Wang et al. (Wang et al., 2015) applied pinewood biochar produced at 600℃ (pH_{PZC} > 7) to absorb As (V) from water at pH 7, with maximum adsorption of 0.3 $mg \cdot g^{-1}$. As (V) mainly existed in the form of $HAsO_4^{2-}$ at pH 7. The biochar surface was positively charged since the solution pH < pH_{PZC}. In that case, $HAsO_4^{2-}$ interacts with the protonated functional groups on biochar surface by electrostatic attraction.

Biochar pyrolyzed from biomass materials has plenty of exchangeable cations on the surface, such as some alkali or alkaline earth metals (Na, K, Mg, Ca) that can be replaced by heavy metal ions during the sorption. Lu et al. (Lu et al., 2012) studied mechanisms for Pb sorption by sludge-derived biochar (SDBC). They found a certain amount of Na^+, K^+, Mg^{2+}, and Ca^{2+} released from SDBC, probably as a result of metal exchange with Pb^{2+}. Zhang et al. (Zhang et al., 2015) studied mechanisms for Cd sorption. They showed that there was almost an equal amount of sorbed Cd and total released cations (Na, K, Mg, Ca) from the water hyacinth biochar, indicating the cation exchange as a leading role in Cd sorption.

Xu et al. (Xu et al., 2016) compared different complexation mechanisms of Hg sorption on bagasse and hickory chip biochar. XPS spectra showed that formation of $(\text{-COO})_2Hg$ and $(\text{-O})_2Hg$ attributed mostly to Hg sorption on bagasse biochar. The sorption capacity decreased by 18% and 38% when using methanol to block the -COOH and -OH functional groups. But the blocking did not affect Hg sorption on hickory chip biochar since the formation of Hg-π binding between Hg and π electrons of C=O and C=C dominated the sorption. Pan et al. (Pan et al., 2013) investigated CrIII sorption on crop straws biochars. The order of their sorption capacity was in accordance with the number of oxygen-containing functional groups, suggesting the importance of CrIII complexation with functional groups in its adsorption on biochar.

Mineral components in biochar are also crucial in the adsorption process, which acts as other adsorption sites and makes contributions to heavy metals adsorption by precipitation (Xu et al., 2013). For example, precipitation was implied to be the dominant mechanism for Cd sorption on dairy manure biochar owing to its relatively high soluble carbonate and phosphate content (Xu et al., 2013). With an increase in temperature from 200 to 350℃, Cd sorption capacity increased from 31.9 to 51.4 $mg{\cdot}g^{-1}$ as a result of the increased mineral content in biochar, especially soluble CO_3^{2-} (from 2.52% to 2.94%). X-ray diffraction following Cd adsorption evidenced that Cd carbonate and phosphate had formed in the biochar (Zhang et al., 2015). Moreover, Trakal et al. (Trakal et al., 2014) used FTIR spectra to follow Cd sorption on biochar with high ash content produced from grape husks and stalks. They suggested that surface precipitation of Cd carbonates have shifted the peaks of CO_3^{2-}. A similar mechanism can be found in the sorption of Pb. Precipitation formation of Pb-carbonate $Pb_3(CO_3)_2(OH)_2$ and Pb-phosphate $Pb_9(PO_4)_6$ contributed most to the high removal rate of Pb (Cao et al., 2009).

Organic contaminants

A series of studies have proved that biochar produced from biomaterials such as agro-processing waste and crop residue has sufficient removal ability for several organic contaminants of concern, such as dyes, pesticides, pharmaceuticals, and phenols (Gwenzi et al., 2017). In general, pore-filling, hydrophobic effect, electrostatic attraction, and hydrogen bonds are the main mechanisms of organic contaminant adsorption on biochar. Specific mechanisms proposed for different types of organic contaminants differ according to the physicochemical properties of the contaminants and biochar.

Pore-filling is an essential mechanism for the sorption of organic compounds on the biochar. The sorption capacity is directly in proportion to the micropores' surface area of biochars (Han et al., 2013). Chen et al. (Chen et al., 2012) reported that the biochar's surface area is affected by pyrolytic temperature, leading to changes in the sorption pH that could strongly influence the surface charge of the uptake rate of a compound. The organic components in the biomass were more completely carbonized at higher temperatures, so the biochar had a higher degree of carbonization. As a result, the biochar obtained a larger surface area and more developed nanopores, achieving an enhanced adsorption rate of Naphthalene (NAP). Zhu et al. (Zhu et al., 2014) reported that large specific surface area and pore volume of carbonaceous materials commonly promote the sorption of organic contaminants as a result of the pore-filling effect. Inyang et al. (Inyang et al., 2014) and Han et al. (Han et al., 2013) also proved this adsorption mechanism in studies of phenol and methylene blue sorption on biochar from aqueous solutions.

Sun et al. (Sun et al., 2013) explored the influence of deashing treatment on the biochar structure and its phenanthrene (PHE) sorption properties. They reported that after deashing treatment, the hydrophobic domains of biochar increased while the polar functional groups decreased, bringing about more favorable hydrophobic adsorption sites for organic compounds, which promoted the PHE sorption. Also, they found that the hydrophobic effect was more significant for biochar prepared at higher temperatures. Ahmad et al. (Ahmad et al., 2013) found that there was a more carbonized portion in the biochar produced under high pyrolytic temperature, resulting in better adsorption for trichloroethylene (TCE). With the increase of pyrolytic temperature, the removal of hydrogen- and oxygen-containing functional groups led to the improvement of hydrophobicity of biochar, thus enhancing the relatively hydrophobic TCE adsorption.

Different results also showed electrostatic interaction to be the primary mechanism of organic contaminant sorption (Inyang et al., 2014). Xu et al. (Xu et al., 2011) studied the sorption mechanism of methyl violet based on adsorption isotherms, FTIR-PAS, zeta potential, and CEC (capillary electrochromatography). They found that electrostatic attraction, to be more specific, the interaction between dyes molecules and -COO- and phenolic -OH groups, promoted the sorption of methyl violet on biochar. Xie et al. (Xie et al., 2014) stated that the sorption of sulfonamides on different biochars is well correlated with the biochars' graphitization degree, and the π-π electron donor-acceptor (EDA) interaction existed between graphitic surface (π electron donors) and sulfonamides (π electron acceptors), accounting for the observed strong adsorption.

Qiu et al. (Qiu et al., 2009) investigated the adsorption mechanism of brilliant blue (KNR) on straw-based biochar. They suggested that the mechanism involved hydrogen bondings. FTIR spectra showed that after KNR adsorption, the intensity of the 1795 cm^{-1} band, which represents C=O stretching shifted little, and the 3447 cm^{-1} band, which represents -OH stretching had a bit change. There was a good chance that the intermolecular hydrogen bonding (O-H- - -O bonds) existed between the H atom in -OH of KNR and the O atom in C=O on biochar surface, vice versa. The negatively charged properties for both biochar and KNR also supported this weak interaction.

The co-existence of carbonized and uncarbonized proportions makes the biochar surface heterogeneous; meanwhile, the two types represent different adsorption mechanisms. In addition to the adsorption of organic compounds onto the carbonized fraction, the adsorption of organic compounds was also governed by partition onto the uncarbonized area (Chen et al., 2008; Cao et al., 2009; Zheng et al., 2010).

Application of biochar in wastewater treatment

Recently, an increased number of reports on adsorption of both inorganic and organic pollutants on biochar has been published. Whether it is directly used in wastewater treatment for different types of wastewater or specific pollutants, or it is used in constructed wetland sewage treatment system or as a soil amendment to improve the quality of the water environment indirectly, biochar has shown favorable treatment effects and has a wide range of applications.

Industrial wastewater

As the dominant source of water pollution, the quantity of industrial wastewater and types of water contaminants are booming due to the rapid development of the industry. Biochar is becoming the new favorite to remove various contaminants from industrial wastewater by virtue of its excellent adsorption ability, both for heavy metals and organic compounds.

Removal of Cd^{2+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cr^{6+} have received more attention due to the adverse effects they could bring if released to the environment and the economic value of recovery at the same time. Batch sorption experiments by Zhou et al. (Zhou et al., 2013) showed that the biochar modified by chitosan had favorable removal efficiency for three heavy metals (Cd^{2+}, Pb^{2+}, and Cu^{2+}) from solution. Further researches of Pb sorption implied that the biochar had a comparatively high Langmuir Pb sorption capability of 14.3 $mg \cdot g^{-1}$, despite the slow sorption kinetics. Xu et al. (Xu et al., 2013) produced dairy manure biochar (DMBC) and rice husk biochar (RHBC) to simultaneously absorb Cd, Zn, Cu, and Pb from water. The results showed that in the removal of all heavy metals, DMBC had the removal ability of over 486 $mmol \cdot kg^{-1}$ for pollutant apiece, which was much better than RHBC (only 65.5-140 $mmol \cdot kg^{-1}$).

With the textile industry expanding rapidly, dye wastewater has become a significant pollution source of water pollution, accounting for a large proportion of industrial wastewater. Based on statistics, there are over 100,000 categories of dyes used in industrial dyeing; however, dyeing manufactories discharge most of the wastewater into the water environment (Dai et al., 2019). Among the methods of dyeing wastewater treatment, adsorption has a broad application prospect compared to other traditional ways (Tang et al., 2017). Scholars especially favor biochar adsorption — for example, Pradhananga et al. (Pradhananga et al., 2017) reported that two dyes used in the wool carpet had very high adsorption capacity on nanoporous biochar derived from bamboo cane. They were lanasyn orange (LO) and lanasyn gray (LG), the adsorption capacity of which are both 2.60×10^{3} $mg \cdot g^{-1}$, assuming that the adsorbate molecules filling into the adsorbent pores were the primary mechanism, and the best adsorption property could be attributed to the high specific surface area (2130 $m^{2} \cdot g^{-1}$) and large pore volume (2.69 $cc \cdot g^{-1}$) of biochar. Researchers produced pecan nutshell biochar to remove Reactive Red 141 from water. The new biochar was claimed to be low-cost and environmental friendly, which could be a substitution to other conventional adsorbents (Zazycki et al., 2018).

Emerging organic pollutants in industrial wastewater, such as phenols and polycyclic aromatic hydrocarbons (PAHs), have gained great concern, while those focusing are comparatively limited. Despite the limitation, Dos Reis et al. (Dos Reis & Dias, 2016) produced biochar from wastewater sludge using two different methods: (i) heating to 500°C under inert atmosphere and (ii) microwave heating under an inert atmosphere, both followed by HCl treatment. Both adsorbents have very high adsorption capability for hydroquinone, which is up to 1218.3 $mg \cdot g^{-1}$ and 1202.1 $mg \cdot g^{-1}$, respectively. π-π interactions and donor-acceptor complex play significant roles in the sorption. Also, the study showed that microwave treatment was an alternative to biochar production. Coal and oil combustion are the primary source of PAHs in the environment. Chen et al. (Chen & Chen, 2009) pyrolyzed orange peel with a temperature range from 150°C to 700°C to make orange peel biochar, which was used to adsorb naphthalene and naphthol. It was found that the biochar prepared at 700°C has a better adsorption effect for naphthalene, while the biochar made at 200°C has a better adsorption effect for naphthol.

Agricultural wastewater

Utilization of pesticides benefits the agrarian production and economy a lot, but the excessive use also causes environmental problems, including air, soil and water pollution, toxicity on non-target organisms, and destruction to ecological balance and human health (Zhong, 2018). Biochar is applied as a distinctive remediation technology considering its favorable properties as an adsorbent and the simplicity of operation in pesticide pollution treatment (Dai et al., 2019). Pesticides treated by biochar include organochlorine, carbamate, chlorophenoxy acid compounds, etc.

Zhang et al. produced maize straw biochar at 300°C, 500°C, and 700°C to study thiacloprid (THI) sorption on it. They found that the adsorption occurred probably via pore-filling, hydrophobic interaction, and π-π interaction (Zhang et al., 2018). Sun et al. (Sun et al., 2018) studied the influences of different factors on the adsorption of organophosphorus pesticide on biochar produced from sugarcane bagasse. They reported that the adsorption process of the pesticide dimethoate was spontaneously exothermic. The higher the carbon content in bagasse, the greater the adsorption capacity, and the better the removal efficiency. Jin et al. (Jin et al., 2016) prepared biochar by pyrolysis of swine manure at 600°C, which was used to for imidacloprid adsorption. The results showed that pore-filling is likely one of the dominant adsorption mechanisms for this kind of polar chemical.

Uchimiya et al. (Uchimiya et al., 2010) and Yu et al. (Yu et al., 2010) produced broiler litter- and red gum wood chips-biochar under different temperatures to remove pesticide and fungicide from water. When the biochar was prepared at above 700°C, because of its large specific surface area, micropores in non-carbonized fraction and aromaticity, the target pollutants can be effectively removed, while the removal efficiency of biochar prepared below 500°C was relatively low. Differently, the removal of polar pesticides and herbicides such as 1-naphthol and norflurazon was owing to specific polar interactions, such as hydrogen bonds between the pollutants and surface functional groups on the biochar.

Klasson et al. (Klasson et al., 2013) prepared almond shell biochar by pyrolysis and steam treatment. The biochar adsorbent had a larger specific surface area of 344 $m^2 \cdot g^{-1}$ and an adsorption capability of 102 $mg \cdot g^{-1}$ for dibromochloropropane (nematode insecticide), and the field experiment was carried out successfully. Zheng et al. (Zheng et al., 2010) investigated the adsorption capacity of atrazine and simazine on biochar. Based on different sorption conditions, the sorption ability of atrazine was 451-1158 $mg \cdot g^{-1}$, and 243-1066 $mg \cdot g^{-1}$ of simazine. When the two adsorbates existed at the same time, there was competitive adsorption on biochar. The adsorption capacity of atrazine was 435-286 $mg \cdot g^{-1}$, and 514-212 $mg \cdot g^{-1}$ of simazine. The study also reported that the adsorption process of single adsorbate, as well as multiple triazine pesticides on biochar, could be well explained by surface adsorption mechanism.

Trace organic pollutants

With the innovations in health care services and products, more people are using drugs to relieve symptoms of various diseases, including antibiotics, anti-inflammatories, and painkillers (Sun et al., 2015). Some antibiotics in pharmaceutical wastewater are difficult to decompose in the natural environment, which will chronically exist in water and soil environment, accumulate in animals and plant bodies, and eventually enter the human body (Islam et al., 2018). Although these antibiotics are generally present at trace concentration ($ng \cdot L^{-1}$ to $mg \cdot L^{-1}$ range), the trace amount is also challenging to degrade in the environment, and it is still unknown about the adverse physiological effects these compounds would bring to wildlife and humans at the trace level (Ebele et al., 2017). Hence antibiotics are also regarded as a kind of emerging environmental pollutant (Carvalho & Santos, 2016), as well as a hot spot in the application of biochar adsorption, with the primary purpose of toxicity reduction rather than reaching the concentration standard of pollutants.

Tetracycline (TC) and sulfonamide (SA) are two of the most commonly used antibiotics and are also used in some intensified agricultural operations as feed additives, which bring potential hazards to the environment and human health when extensively used (Yu et al., 2016; Shao et al., 2005). The removal of TC by Fe-Zn mixed sawdust biochar was studied systematically. The results showed that this kind of biochar had the potential ability for TC removal in water, with the removal rate above 89.00% after three cycles (Zhou et al., 2017). Peiris et al. (Peiris et al., 2017) made a further study on the adsorption mechanisms of SAs on biochar. Generally, high temperature produced biochar (HTBC) showed high adsorption quantity under the condition of weak acidity, which is because the strong EDA interaction occurs between the abundant arene rings on the biochar surface (π electron donors) and the SAs (π electron acceptors). Micropore-filling is also a common mechanism because of the smaller size of SAs.

Besides antibiotics, there are novel but limited studies on the removal of indicator organisms and pathogens by biochar in aqueous solution. For example, researchers studied the anaerobic biofiltration of rice husk biochar and non-pyrolyzed rice husk as low-cost filter materials for wastewater, and evaluated their potential and limitation, to promote the food safety in developing countries (Kaetzl et al., 2019). The filters ran over a year to collect sufficient and detailed data on their performances. In general, the performance of the biochar filter was superior or equal to the rice husk and sand filters. The treated wastewater was then used in a pot test for lettuce irrigation, and the results showed that the contamination with the fecal indicator bacteria (FIB) was >2.5 log-units lower than the lettuce irrigated with untreated wastewater. Similarly, researchers showed that by using biochar as a filter medium, >1 log_{10} CFU Saccharomyces cerevisiae was successfully removed from diluted wastewater under the condition of on-farm irrigation. The particle size of biochar is the main influencing factor accounting for the microbial removal efficiency. The minimum particle size (d_{10} = 1.4 mm) could consistently remove at least 1 log_{10} CFU of most target microbes. More micropores and smaller pore sizes could increase the straining effect and the contact time between bacteria and sorption sites. This treatment by biochar for wastewater-polluted streams provides a novel method for safer irrigation in developing countries.

Inorganic ions

Ammonium (NH_4^+) is an emerging contaminant that can bring present considerable risks to natural ecosystems. Volatilization of ammonium can restrain the photosynthesis of algae through electron transfer and chlorophyll fluorescence. Excessive ammonium in fishing ponds can cause gill injury and brain swelling to the fish and damage the respiratory metabolism. Therefore, it is necessary to develop effective ammonium control technology in the water environment (Fan et al., 2019).

Fan et al. (Fan et al., 2019) conducted a study focused on adsorption characteristics of NH_4^+ on hydrous bamboo biochar. The results found that the bamboo biochar had a sufficient adsorption capacity for ammonium ions, with a maximum of 6.38 $mM \cdot g^{-1}$. The adsorption was enhanced at higher ionic strength conditions, indicating that physical reactions possibly made contributions to the adsorption process, such as electrostatic interaction and surface precipitation. Xu et al. (Xu et al., 2019) studied the characteristics and NH_4^+ sorption ability of biochars produced from various raw materials (eggshell, rice straw, Phragmites communis, and sawdust) under different pyrolysis temperatures. The highest NH_4^+ adsorption appeared in rice straw biochar produced at 500℃ (4.2 $mg \cdot g^{-1}$). The results suggested that the C/H ratio and zeta potential of biochar have more decisive impacts on NH_4^+ adsorption potential, instead of the specific surface area.

Vu et al. (Vu et al., 2017) did research focusing on corncob biochar as a low-cost adsorbent, and evaluated its efficiency for NH_4^+ removal from simulated water solutions (NH_4^+ concentration ranged from 10 to 100 mg·L^{-1}). They found that the sorption strongly depended on the solution pH. The highest sorption capacity (22.6 mg NH_4^+-N/g biochar) suggested the biochar to be a prospective adsorbent for NH_4^+-N removal from wastewater.

As a result of excessive use of fertilizers and manure in agricultural activities and discharge of domestic sewage, the abundance of N and P causes eutrophication in water, consequently leading to a deterioration of the water environment. Besides the conventional biochemical technologies for water eutrophication treatment, physical sorption is a convenient and straightforward method without causing secondary contamination (Yang et al., 2018; Yin et al., 2017). The maximum equilibrium sorption capacity of NO_3^- (95 mg·g^{-1}) was associated with MgO-modified sugar beet tailing biochar, owing to its highly porous structure comprising of MgO nano-flakes in the biochar matrix (Zhang et al., 2012). Walnut shell and sewage sludge were co-pyrolysed to produce biochar for the sorption of phosphate from eutrophic water (Yin et al., 2019). The biochars exhibited ideal sorption ability for PO_4^{3-}. Pure sewage sludge biochar (SBC) had the maximum adsorption capacity reaching 303.49 mg·g^{-1} in a wide pH range and was the best option for PO_4^{3-} adsorption among the biochars. Excessive fluoride in drinking water (WHO guideline = 1.5 mg·L^{-1}) can lead to fluorosis in dens and skeleton, ossification of ligaments and tendons, neurological disorders, and rickets, which is responsible for growth disorder and intelligence decline (Dong & Wang, 2016). A study has found that the aluminum-modified Scandinavian spruce wood biochar had a maximum removal capability of 13.6 mg·g^{-1} for the fluoride ion. The dispersion of aluminum into the porous structure of biochar significantly increased the adsorption (Tchomgui-Kamga et al., 2010). The Langmuir isotherm adsorption model served as the most suitable model for the adsorption and removal of fluorine ion pollutants on biochar from water (Ahmed et al., 2016).

Indirect wastewater treatment fields

In recent years, constructed wetlands (CWs) have been widely used in contaminants removal, including nitrogen (N), phosphorus (P) (Li et al., 2019), and some organics in wastewater. Nevertheless, due to the limited oxygen supply and transport capacity, as well as the adsorption capacity of the substrate and the inhibition of microorganisms and plants at low temperatures, the removal efficiency of CWs for N and P is severely hindered (Ying et al., 2010). To efficiently treat wastewater with high pollutants concentration, many pieces of research have attempted to explore particular substrates. Nevertheless, due to the sludge production, the complex regeneration process, and the cost, it is difficult to maintain the sustainability of this kind of CWs (Feng et al., 2020). In recent years, due to the advantages of large specific surface area, porous structure, and functional cation exchange capacity, biochar has been more and more used as the substrate of CWs (Gupta et al., 2015).

Zhou et al. (Zhou et al., 2018) used biochar as a substrate in vertical flow constructed wetlands (VFCWs) to enhance the adsorption and removal efficiency of contaminants from wastewater with a series of low C/N influent strengths. They systematically assessed the removal performance of nitrogen and organics in both biochar-added and non-biochar-added VFCWs. The results showed that compared with traditional VFCWs, the average removal rate of NH_4-N (39%), TN (39%), and organic pollutants (85%) were better than those of conventional VFCWs, especially for the high-strength wastewater. Therefore, it is believed VFCWs with biochar adding into the substrate is a useful technology for the treatment of low C/N ratio wastewater. A seven-month study clearly showed that enriched biochar is a suitable substrate for phosphorus removal and retention (Bolton et al., 2019). The removal efficiency of PO_4-P in wetlands with biochar added was significantly higher than that in the control wetland. This spent biochar can also be applied as soil fertilizer for soil improvement with regeneration potential, but this application still needs more research.

Gholami et al. (Deng et al., 2019) constructed four subsurface flow constructed wetlands (SFCWs) to assess the characteristics of microorganisms and their metabolites with biochar additive based on the biochar volume ratio in standard gravel (0%, 10%, 20%, and 30%). Results indicated that the removal rate of ammonium and total nitrogen by SFCWs with biochar was higher than that by pure gravel filled SFCWs. The addition of biochar can promote the removal efficiency of nitrogen by changing the structure of the microbial communities and increasing the relative abundance of dominant species. Besides, biochar can also improve the metabolism of high molecular compounds and convert them into low molecular compounds. These results provided new insights into strengthening nitrogen removal by the metabolism of microbes with the effect of biochar.

Besides, in the field of watershed treatment, biochar has shown the potential for restoration of soil hydraulic properties. Bayabil et al. (Bayabil et al., 2015) carried out laboratory and field experiments in the Anjeni watershed in the Ethiopian highlands to measure the soil's physical properties such as infiltration rates and moisture retention. They concluded that the addition of woody charcoal (derived from eucalyptus, acacia, and croton) and biochar (derived from oak) could improve the physical properties of degraded soils (such as hydraulic conductivity), thereby reducing runoff, erosion and waterlogging in the field. Gholami et al. (Gholami et al., 2019) studied the overall effects on the water conservation in eroded soil caused by initial soil humidity and the addition of biochar produced from poultry sewage sludge. The results implied that the application of biochar increased the runoff time while decreased the runoff coefficient, soil erosion, and sediment concentration, which could be an economical, effective and safe method to reduce soil surface runoff, soil erosion, sediment concentration, and the environmental water contaminants as well.

Although biochar has extensive use in the removal of diversiform contaminants in wastewater (Vithanage et al., 2015), its applicability is still limited to some extent because of its lower removal efficiency for some select pollutants or in some specific water conditions. The unmodified biochars have much lower removal ability than the modified ones, especially in high-strength wastewater (S & P, 2019). Therefore, researchers have paid attention to the modification of biochar with better surface properties and novel structures to improve its removal ability and environmental profits (Rajapaksha et al., 2016).

Modification of biochar

Researchers have found a relationship between the surface area and functionality of biochar and the adsorption capacity of pollutants (Goswami et al., 2016; Tan et al., 2015). The broad distribution of micropores and mesopores makes contributions to a higher specific surface area of the biochar. More micropores correspond to larger surface area and more adsorption sites where contaminants can be adsorbed (Sizmur et al., 2017). Accordingly, the objectives of the treatment are generally concerning (i) increase of specific surface area, (ii) enhancement or modification of surface properties, or (iii) embedding other materials into biochar surface to obtain beneficial surface properties (Sizmur et al., 2017). The purpose of the modification is to enlarge the biochar's surface area or to improve the activity of the original functional groups, while the modification focuses more on changing the surface properties of biochar, such as introducing some new functional groups with specific functions that do not previously exist. According to the different modification emphasis, the modification methods of biochar are summarized in Figure 2. Modification of biochar increases the breadth of chemical pollutants, which can be manipulated due to the enhanced sorption properties.

Increase of specific surface area

In general, biochar with more micropores, larger surface area, and pore volume usually have more adsorption sites, which contribute to a better sorption capacity. Researchers have proposed various ways for the modification of biochar to gain favorable sorbents with the benefits above.

Physical modification usually uses gases such as CO_2 (Guo et al., 2009) and steam (Shim et al., 2015) to treat biochar at the temperature over 700℃. Under the action of steam, the pore structure of biochar increased, and the incomplete combustion components are removed, both of which increase the adsorption sites. Lima and Marchall (Lima & Marshall, 2005) used poultry manure as feedstock to produce biochar at 700°C. Then the biochar was treated under a series of steam with different water flow rates and durations at 800°C. The results showed that longer action times and higher flow rates increased the adsorption of Cu, Zn, and Cd on the biochar surface. Zhang et al. (ZHANG et al., 2004) investigated the effects of temperature and duration of CO_2 treatment on properties of biochars derived from corn stover, corn hulls, and oak wood waste. All three biochars exhibited an increase in specific surface area and micropore volume with the growth of the temperature even though steam treatment raised the specific surface area and pore volume, Lou et al. (Kangyi Lou, 2016) claimed that the steam treatment had no significant effect on surface functional groups on biochar. Therefore, the steam treatment appears to be more efficient if it is used before a second modification step, which can increase the enrichment of surface functional groups (Sizmur et al., 2017).

Acidic or alkaline treatment also has effects on increasing the surface area. Zhao et al. (Zhao et al., 2017) treated pine tree sawdust with diluted H_3PO_4 before pyrolysis. Both of the total surface area and pore volume increased after the treatment. The P-O-P bonds were incorporated into the C structure, and the adsorption ability for Pb increased by more than 20% because of surface adsorption and phosphate precipitation, compared with the untreated sample. Goswami et al. (Goswami et al., 2016) proved that treating biochar with KOH followed by pyrolysis at 350-550°C reopened some of the blocked pores, and expanded the pore size of the smaller pores, increasing the surface area and Cd sorption from the water via the surface complexation mechanism. Hamid et al. (Hamid et al., 2014) reported that the increase of surface area resulting from KOH modification also increased the sorption of oxyanions. For that, Jin et al. (Jin et al., 2014) proposed that the maximum As(V) sorption on biochar derived from municipal solid wastes (MSW) with KOH modification increased by 1.3 times, from 24 $mg \cdot g^{-1}$ to 31 $mg \cdot g^{-1}$, as a result of increased surface area. In addition, the researchers had found a larger surface area and higher iodine adsorption capacity of both the feedstock and the biochar when the modification was conducted by physical mixing with solid NaOH (Pietrzak et al., 2014).

Besides the methods mentioned above, some other modification methods of biochar also enhance the adsorption by increasing the surface area. The preparation of biochar-based composites is a common way for biochar modification, by impregnating biochar with specific materials, to change the surface properties of biochar. In this case, the biochar primarily played a role as a scaffold with the high surface area on which other materials are deposited (Sizmur et al., 2017). Chen et al. (Chen et al., 2017) pointed out that blending the bamboo powder with montmorillonite before pyrolysis led to an increase in the specific surface area and porosity, partially as a result of the existence of layered montmorillonite, which contributed to a better sorption capacity for NH_4^+ and PO_4^{3-}, compared with the unmodified biochar. Yao et al. (Yao et al., 2014) have observed the layered surfaces of clay modified biochar through Scanning Electron Microscope (SEM) imaging, similar to a typical clay structure morphology.

Increase of positive surface charge

Biochar usually has a high specific surface area, but the surface charge is generally negative and has a higher pH value. These properties make biochar an excellent material for adsorption of metal cations. The adsorption mechanism mainly includes precipitation on the mineral components in biochar, electrostatic attraction between the target pollutants and aromatic groups, and adsorption on oxygen-containing groups. However, the biochar seems to be poor adsorbents for oxyanion such as NO_3^-, PO_4^{3-} and AsO_4^{3-} (Sizmur et al., 2017). The modification usually uses the porous surface of biochar as a scaffold for embedding positively charged metal oxides. The obtained composite can remove oxyanions with the negative charge from water (Sizmur et al., 2017).

Most methods to prepare metal oxide-biochar composites aim to assure that the metal is homogeneously distributed on the biochar surface. Just like other conventional biochar-based composites, the biochar here plays a role as porous carbon support where the metal oxides precipitate to gain more positive surface charge and surface area simultaneously. In general, biochar or the raw materials were soaked into metal chloride or nitrate solutions ($MgCl_2$, $FeCl_3$, $Fe(NO_3)_3$ and Fe^0 are most frequently used) to realize the attachment of metals, followed by a heating under atmospheric conditions at the temperature of 50-300℃, to make the chlorides or nitrates be driven off as Cl_2 and NO_2 gases and turn the metal ions into metal oxides (Sizmur et al., 2017). Zhang et al. (Zhang et al., 2012) used five common biomass feedstocks (sugarcane bagasse, sugar beet tailings, cottonwoods, peanut shells, and pine woods) to create biochar-MgO composites by mixing the feedstocks with $MgCl_2$-$6H_2O$ and then pyrolyzing. The scanning electron microscope (SEM) showed that the MgO particles were uniformly spread on the biochar surface. The maximum sorption capacity for nitrogen and phosphorus from sewage reached 95 and 835 $mg \cdot g^{-1}$, respectively, due to positively charged MgO that precipitated onto the biochar. They also produced biochar/MgAl-LDH (layered double hydroxides) by mingling cotton stalk with a mixed solution of $AlCl_3$-$6H_2O$ and $MgCl_2$-$6H_2O$ (Zhang et al., 2013). The maximum adsorption capacity for phosphorus increased by 5-50 times surfaces.

Biochar based composites can also be prepared by embedding Al, Mn or Mg oxides onto the biochar surface, which can improve the adsorption of both oxyanions and metal cations (mainly Pb). Jellali et al. (Jellali et al., 2016) explored the potential effect of Mg modification on increasing the adsorption for metal cations. In this study, the Pb sorption from solution by an $MgCl_2$-treated pyrolyzed biochar and the unpyrolysed raw cypress sawdust was investigated. Results gave the maximum sorption capacity of the former, which was about 7.4 times more than that of the latter.

In general, the sorption of oxygen-containing anions on the surface of biochar-based metal oxide composites arises from electrostatic attraction or chemical sorption with positively charged metal oxides in the biochar matrix (Ren et al., 2015; Zhou et al., 2014), while the sorption mechanisms of metal cations involve co-precipitation occurring in the metal oxides lattice, or chemical sorption on oxygen-containing functional groups on biochar’s unmodified part (Tan et al., 2015). Rajapaksha et al. (Rajapaksha et al., 2016) suggested that even though most modifications by metal oxides lead to a decrease in the specific surface area because of pore-clogging with the metal oxide precipitates, the modifications eventually increase the sorption capacity owing to the formation of pH-dependent bindings with the positively charged functional groups on the surface of biochar.

Enhancement of the activity of surface oxygen-containing functional groups

The biochar surface contains several functional groups, such as phenol, carboxyl, and hydroxyl, which are capable of chemically bonding with contaminants and remove them from aqueous solutions.

The acid treatment provides additional oxygen-containing functional groups on the surface of biochar and increases the potential of chemically bonding with positively charged contaminants via specific adsorption. The biochar forms carboxylic groups on its surface when exposed to acidic solutions (Hadjittofi et al., 2014; Qian et al., 2013). Hadjittofi et al. (Hadjittofi et al., 2014) used HNO_3 to modify biochar produced from cactus fibers to obtain more surface carboxyl groups, which play the role of influential sorption sites for metal cations (such as Cu^{2+} and Pb^{2+}). The adsorption capacity at pH 6.5 was an order of magnitude larger than that at pH 3, indicating the pH-dependent and chemical adsorption on oxygen-containing functional groups on the surface. Qian et al. (Qian et al., 2013) suggested that after the treatment in a mixture of H_2SO_4 and HNO_3, the O/C ratio of rice straw-based biochar was higher in the final product, implying that oxygen-containing functional groups were incorporated in the biochar's structure.

Since the modification of biochar by strong acids is costly in the large-scale application and the environmental concerns that exist along with the disposal of the modification reagent, researchers have made efforts to come up with cheaper and cleaner oxidants as alternatives to modify biochar. Song et al. (Song et al., 2014) pyrolyzed corn straw at 600℃ and then mixed it with the $KMnO_4$ solution. A MnO_x-biochar was prepared after another pyrolysis. Compared with the original biochar, the O/C ratio increased from 0.04 to 0.53. X-ray photoelectron spectroscopy (XPS) analysis showed that the increased oxygen existed mainly in the Mn-OH and Mn-O structure, which primarily accounted for the enhanced adsorption ability for Cu^{2+} (from 19.6 to 160.3 $mg \cdot g^{-1}$). Huff and Lee (Huff & Lee, 2016) reported that there was an increase in the number of oxygen-containing functional groups on the biochar surface after treatment using H_2O_2. The cation exchangeability of the biochar was almost doubled than that of an untreated one, as a result of cation exchange on the more abundant oxygen-containing functional groups on modified biochar's surface.

Alkaline solutions play a similar role to acids and oxides in increasing the number of oxygen-containing functional groups on the surface of biochar. Jin et al. (Jin et al., 2014) reported that the KOH modification of municipal solid wastes biochar enhanced the As(V) adsorption performance, not only due to the increase in surface area, but also owing to the growing number of surface oxygen-containing functional groups. These functional groups provided proton-donating exchange sites where metal cations can be chemically absorbed (Petrović et al., 2016).

Among various biochar-based composites, biochar-based carbonaceous materials show similar properties of increasing oxygen-containing functional groups on the sorbent surface. The graphene oxide-biochar composite material is obtained by impregnating the raw material in a graphene oxide suspension and then pyrolyzing. After pyrolysis, the incorporation of the graphene structure generally produced more oxygen-containing functional groups (Shang et al., 2016; Tang et al., 2015). The removal rate of Hg^{2+} raised with the increase of the proportion of graphene oxide in the composite. When the maximum percentage of graphene oxide is 1%, the removal rate of the composite was 8.7% more than that of the unmodified biochar. Results of Fourier transform infrared spectroscopy showed that the abundance of oxygen-containing functional groups dominantly bound the adsorption behavior of Hg^{2+} on graphene oxide-biochar composite.

Incorporation of surface amino functional groups

Incorporation of amino functional groups onto the biochar surface can improve the adsorption ability through inducing strong complexation between pollutant molecules and amino moieties. The modification is obtained either by simple chemical reactions (Yang & Jiang, 2014) or mixing biochar with amino-rich polymers such as polyethyleneimine or chitosan (Ma et al., 2014; Zhou et al., 2014; Zhou et al., 2013).

Yang and Jiang (Yang & Jiang, 2014) used HNO_3, H_2SO_4, and $Na_2S_2O_4$ to modify biochar as a selective and efficient sorbent for Cu^{2+} by nitration and reduction. Although there was little significant difference in the physical structure before and after the modification, ATR-FTIR and XPS results showed the amino groups chemically binding to the functional groups on the surface of biochar. The amino modification made the adsorption capacity for Cu^{2+} increased by five times. Ma et al. (Ma et al., 2014) used polyethyleneimine (PEI) to prepare amino groups-rich biochar to remove Cr(VI) from aqueous solutions. FTIR and XPS characterized the biochars before and after modification. The maximum sorption capacity (435.7 $mg \cdot g^{-1}$) was much higher than that of the unmodified biochar (23.09 $mg \cdot g^{-1}$).

Zhou et al. (Zhou et al., 2013) synthesized chitosan-modified biochars derived from peanut hull, hickory wood, sugarcane bagasse, and bamboo for the aim of providing a commercial sorbent for heavy metal remediation in the environment. Characterization of the biochars showed that the chitosan coating on the surface of biochar improved the surface properties. Batch sorption experiments stated that the removal ability for Cd^{2+}, Cu^{2+}, and Pb^{2+} in aqueous solution by almost all chitosan-modified biochars was enhanced, compared with the unmodified biochars. Further studies of Pb adsorption on chitosan-modified bamboo biochar found that, even though the adsorption kinetics were slow, the modified biochar had a relatively high Langmuir Pb adsorption capability of 14.3 mg adsorbate per gram of biochar, significantly reducing the toxicity of Pb. Characterization of the Pb-loaded biochars after sorption exhibited that the sorption of Pb is primarily caused by the interaction with amino functional groups on the surface.

Other modification methods

The magnetization of biochar adsorbent is a new modification methodology. Utilization of a magnet enables the biochar that is loaded with pollutants to be removed from the media, overcoming the difficulty of the separation of non-magnetic adsorbents.

Several studies have tried to use the magnetic properties of Fe to prepare magnetic biochars (Mohan et al., 2014; Zhou et al., 2014). According to current studies, most researchers choose to mix the suspension of prepared biochar with Fe^{3+}/Fe^{2+} solution to get magnetic biochar. In this way, Mohan et al. (Mohan et al., 2014) first produced biochar from oak wood and bark. It was found that the iron content of the two biochars increased from 1.40% to 80.6% and 0.21% to 51.3%, respectively, indicating that the biochars were effectively magnetized. In the application of Pb^{2+} and Cd^{2+} removal from solutions, results showed that the saturated adsorption capacities of magnetic biochars were significantly higher than those of biochars without magnetization. Devi et al. (Devi & Saroha, 2014) synthesized zero-valent iron magnetic biochar composite. FTIR found that the number of functional groups (carboxyl, alcohol hydroxyl, etc.) on the surface had increased after the magnetization. Consequently, the removal efficiency for pentachlorophenol (PCP) from wastewater was improved remarkably.

Especially, taking advantage of the high surface area and inert property, biochar can be used as a scaffold for colonization and growth of biofilms with ideal features. The primary purpose of inoculating microbes on the biochar surface is to promote the biodegradation of organic pollutants (Sizmur et al., 2017); however, alongside the function of biodegradation, Frankel et al. (Frankel et al., 2016) observed the growth of bio-films by microorganisms isolated from oil sand process wastewater onto the biochar surface, and the adsorption of metals from the solution. The adsorption capacity of P and As was 6 and 7 times higher than that of the uncolonized biochar and was 4 and 5 times higher than that of the uncolonized but sterilized biochar.

Environmental concerns and future work

In general, biochar is not yet widely applied and still in the test stage of researching. At present, the production and application of biochar have not attracted enough attention, especially in some developing countries where the complete industrial chains are lacking. Besides, many environmental concerns cannot be ignored in the practical application of biochar. In this case, a large amount of research work needs to be carried out to solve the potential environmental problems in the process of biochar applying and to provide the developing countries with specific research programs on biochar technology, including the sub-Saharan African countries (Gwenzi et al., 2017) to popularize the application of biochar. The potential environmental concerns and the propositional future research directions on the proposed issues are as follows:

Although the feedstock for biochar is extensive and easy to obtain, these raw materials need to be prepared (cleaning, drying) and then pyrolyzed for the available biochar. The modification step is also required to improve the adsorption effect. Compared with conventional activated carbon, these treatments for biochar will inevitably increase the costs of production costs. Therefore, investigation on optimizing the production process is critical for producing biochar with the necessary properties and minimum costs. A large number of existing research results can be accumulated to summarize the excellent raw materials and production conditions, which significantly affect biochar's quality with specific functions. For example, because of the resistance of lignin, the micropore area of lignin biochar (200 $m^2 \cdot g^{-1}$) was less than that of the cellulose biochar (280 $m^2 \cdot g^{-1}$) carbonized at the same temperature, showing that cellulose biomass is preferable for the production of high-quality biochar than lignin biomass; the specific surface area and total pore volume of pinewood biochar pyrolyzed at 600℃ were 368 $m^2 \cdot g^{-1}$ and 0.19 $cm^3 \cdot g^{-1}$, respectively, which were much higher than the biochar pyrolyzed at 400℃ (33.3 $m^2 \cdot g^{-1}$ and 0.022 $cm^3 \cdot g^{-1}$, respectively), due of the incomplete carbonization of the lignin at 400℃ resulting in the not well developed pore structure (Li et al., 2014). Future developments should attempt to find a compromise among feedstocks, production methods, and adsorption properties and aim to obtain multifunctional biochars with predictable properties, to minimize the production cost and maximize the applicability and performance of biochar products (Sizmur et al., 2017).

The stability of biochar is a valuable property that should be considered in the process of biochar application. Biochars are highly heterogeneous materials (Gwenzi et al., 2017) and are mainly constituted of the carbon structure. The biochar stability generally refers to the stability of its carbon structure (Wang & Wang, 2019). Huang et al. (Huang et al., 2019) investigated the possible dissolution of organic matters from biochar in the process of complexation with heavy metals, indicating that the instability of biochar can lead to the occurrence of organic matters in the solution. Besides, the dissolved organic matters may have high aromaticity and stability, which increase the carbon content in the water when biochar is applied in wastewater treatment. Moreover, the biochars, especially those derived from sludge, could contain high heavy metals that could be leached out during the wastewater treatment, causing heavy metal pollution (Wang & Wang, 2019). Thus, the stability of biochar is bound up with the wastewater treatment efficiency and water quality, which still needs more research work. The content and structures of carbon in biochar is a vital parameter of biochar stability. In consideration of the impact of the carbonization method on carbon content and structure, it is necessary to study the relation between biochar stability and carbonization conditions. For example, biochar produced via hydrothermal carbonization possesses higher carbon content than that via gasification and pyrolysis (Funke & Ziegler, 2010). More investigation may be made in hydrothermal carbonization technology in the future. Besides, to facilitate the practical application of biochar, toxicity tests using water fleas, fish, alga, or luminous bacteria (Wang & Wang, 2019) are needed to measure the toxicity of biochar-applied wastewater to determine whether toxic components are dissolving from the biochar.

The stability of biochar-based composites is another concern. Considering that the biochar here just acts as a scaffold and are impregnated with carbonaceous materials, organic compounds, clays, metal oxides, etc. to make them imbibed in the biochar matrix, there is possibility that some of the materials leach out from the biochar if they are not well-fixed, resulting in additional water pollution. In this case, in future experiments, the stability of biochar-based composites during its application should be monitored. For solving this problem, leaching tests are required. For example, a worthy study is carried out to investigate the stability of metal-biochar composites in acidic solution (pH 4-5) to make sure if the metal could release from the biochar matrix (Sizmur et al., 2017). These studies are of guiding significance for the synthesis conditions and adsorption environment of the composite sorbents.

Most researches have focused on the adsorption of single pollution in aqueous solutions. However, in practical application in real water, the prevailing situation is the coexistence of a variety of pollutants. As the adsorption involves multi-component systems, synergistic and antagonistic effects can be observed. The presence of multiple pollutants could potentially result in ionic interference as well as the competition of sorption sites and eventually reduce the removal efficiency. Besides, ionic species, ionic strength, and pH make the sorption process more complex (Gwenzi et al., 2017). At present, empirical data based on adsorption in the multi-pollutant system is minimal. Therefore, the development and verification of models suitable for the simultaneous sorption process of various pollutants will become a critical advance (Gwenzi et al., 2017). To achieve this goal, the literature on biochar sorption should include the information of adsorbents characterization and adsorption conditions as detailed as possible, to provide directions for more complex research. Bahamon et al. (Bahamon et al., 2017) reported the use of simulated molecular equations for studying competitive adsorption of multi-component systems. In future research, new analysis methods can be carried out, such as meta-analysis (Wang et al., 2019) and in-depth analysis (Tran et al., 2019; Feng et al., 2016) to study the possible new adsorption model.

Although it is generally recognized that compared with activated carbon, biochar is low-cost, renewable, and sustainable (Mohan et al., 2011), to achieve regeneration and sustainability, it is necessary to solve the problem of recovery and disposal of the adsorbed biochar. A method worthy of further study is the magnetization of biochar, which makes it accessible to separate the pollutant-loaded biochar from water by applying an external magnetic field. As for the disposal, a considerable challenge is how to get desorption and recover the pollutants from the surface of biochar so that it can be put into use again. The desorption process may cost a lot. On the other hand, if pollutants absorbed on biochar cannot be effectively desorbed and recovered, it is also feasible to use the saturated biochar as a resource. For example, biochar laden with N and P can be of potential use as a slow-release fertilizer in agriculture or ecological remediation (Roy, 2017). Accordingly, biochar laden with Cu or Zn can be used as a micro-nutrient fertilizer as well. Nevertheless, attention should be paid whether any harmful components could release from the biochar, which would be absorbed by crops and consequently enter the food chain. Therefore, the safety of applying waste biochar into soil needs to be further evaluated.

Conclusions

Biochar has shown excellent advantages and is widely used in industrial, agricultural, and pharmaceutical wastewater treatment to remove common organic and inorganic pollutants, as well as the emerging trace persistent pollutants. Biochar utilization in constructed wetlands (CWs) and watershed is also expanding. Present studies focus on improvements in specific surface area or surface properties of biochar, or research and development of beneficial biochar-based composites, aiming at enhancing its adsorption ability. Meanwhile, remaining environmental concerns about biochar application cannot be ignored. The stability and toxicity of biochar and its composites, the adsorption behavior in complex water bodies of multiple pollutants, the disposition of waste biochar, along with the full range economic effects are the future emphases and research directions to facilitate the practical application of biochar in wastewater treatment.

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Figure 1

Summary of dominant mechanisms involved in contaminants removal on biochar.

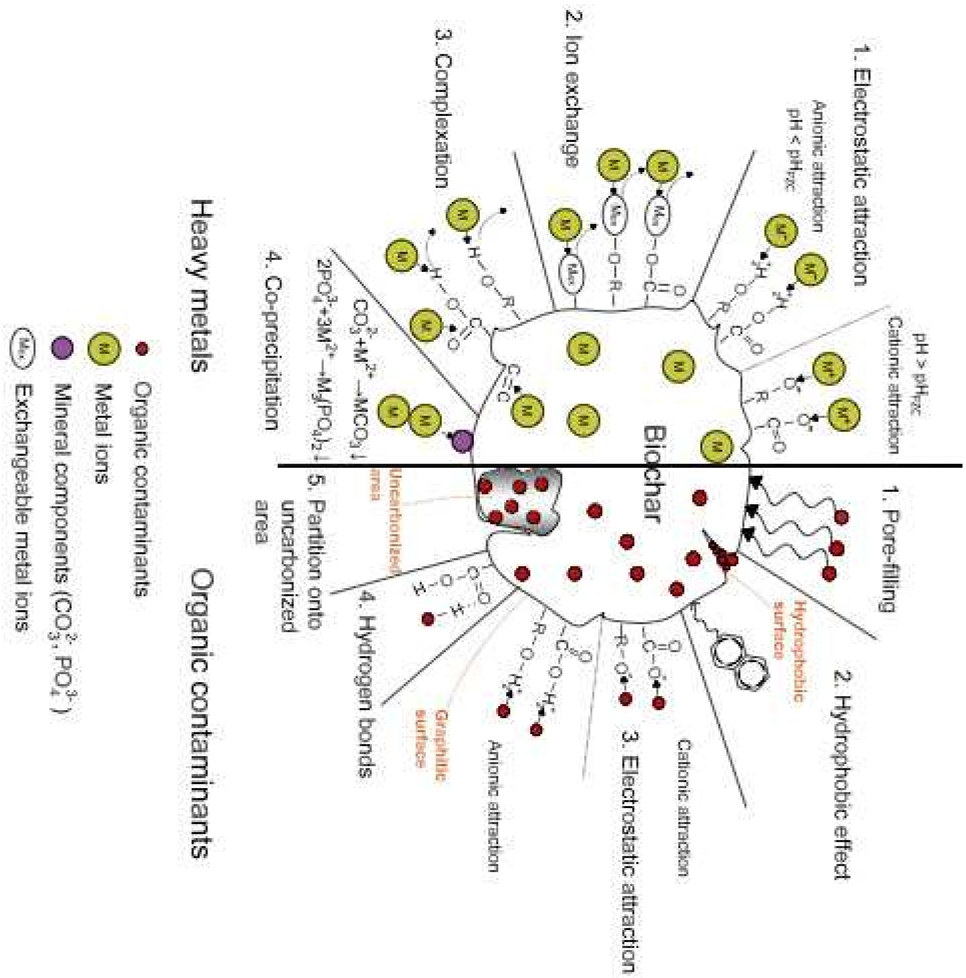
Biochar
Heavy metals
1. Electrostatic attraction
Anionic attraction
pH < pH$_{PZC}$
pH > pH$_{PZC}$
Cationic attraction
2. Ion exchange
3. Complexation
4. Co-precipitation
$CO_3^{2-}+M^{2+}\rightarrow MCO_3\downarrow$
$2PO_4^{3-}+3M^{2+}\rightarrow M_3(PO_4)_2\downarrow$
Organic contaminants
1. Pore-filling
2. Hydrophobic effect
Hydrophobic surface
3. Electrostatic attraction
Cationic attraction
Anionic attraction
Graphitic surface
4. Hydrogen bonds
5. Partition onto uncarbonized area
Uncarbonized area
Organic contaminants
Metal ions
Mineral components (CO_3^{2-}, PO_4^{3-})
Exchangeable metal ions

Figure 2

Biochar modification methods based on different concerns.